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(54) Improved process for the production of edible oils.

(57) The present invention relates to an improvement to a hydrogenation process for the production of moderate and high selectivity edible oils which results in a reduction in the required catalyst and in hydrogen consumption. The improvement comprises the use of high purity hydrogen (i.e. from a liquid hydrogen source); the use of a predetermined catalyst concentration, reaction starting temperature, and maximum temperature which is determined by product selectivity; and the use of reactor venting in relationship to the concentration of moisture in the feedstock and the gas mixing mechanism in the reactor.

FIG. 3

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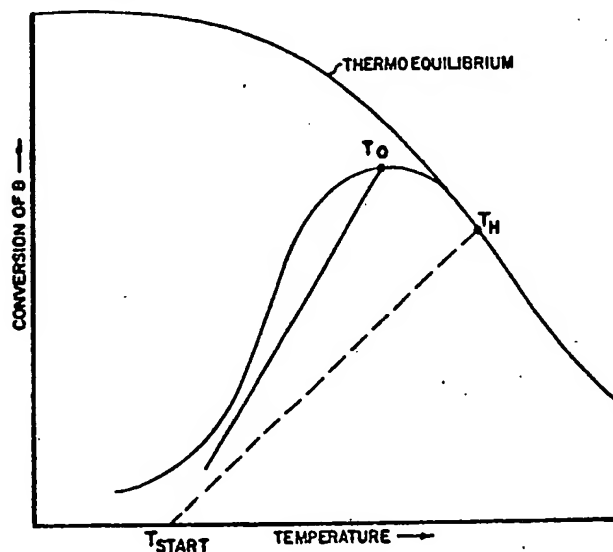
IMPROVED PROCESS FOR THE PRODUCTION OF EDIBLE OILS

FIELD OF INVENTION

5   The present invention relates to an improvement to a hydrogenation process for the production of edible oils.

BACKGROUND OF THE INVENTION

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There are several processes in the art which teach the hydrogenation of unsaturated oils to produce moderate and high selectivity edible oils, among these are the following:

U.S. Patent No. 4,584,139 discloses that an improved monolithic hydrogenation catalyst and processes
15 for using same to hydrogenate animal and vegetable oils, said catalyst being comprised of a Raney metal alloy surface layer integral with and derived from a selected nickel alloy monolithic substrate mesh structure wherein said surface layer is predominantly derived from an adherent Beta structured crystalline presursor outer portion thereon. The catalyst is adaptable to both continuous and batch hydrogenation and shows enhanced activity, improved triene to diene selectivity and a low isomerization index. Hydrogenated oils
20 show lower linolenic and stearic contents, lower trans-isomer percentages and lower melting points as compared to commercial products of equivalent iodine number.

U.S. Patent No. 4,666,635 discloses a process for the catalytic hydrogenation of an unsaturated compound using nickel-silica catalyst. The catalyst comprises aggregates which have an average particle size ranging from 2 to 100 micrometers and said aggregates have outer surface which is at least 60% free
25 of carrier particles.

U.S. Patent No. 4,307,026 discloses a hydrogenation process in which an unsaturated fatty acid derivatives which, besides fatty acids with two double bonds, contain fatty acids with more than two double bonds, are hydrogenated in the presence of a palladium, platinum or rhodium catalyst which has been treated with ethylenediamine or a homologue and/or a derivative thereof and at a temperature of -20° to
30 100° C. The hydrogenation progresses very selectively while very little isomerization to trans-fatty acids occurs.

For example, in the hydrogenation of soya bean oil to a linolenic acid content of 2%, the linoleic acid content only decrease to 45-52%. under identical conditions an untreated catalyst leads to a linoleic acid content of about 35%.
35   U.S. Patent No. 4,385,001 discloses that edible oils may be selectively hydrogenated using a zerovalent, supported, catalytically active cobalt catalyst. While the cobalt is supported on alumina, the selectivity of hydrogenation is virtually independent of the nature of the alumina. The process is sufficiently selective that continuous hydrogenation may be performed with about the same selectivity as that presently obtained in batch processes using presently conventional catalysts.
40   U.S. Patent No. 4,424,163 discloses that selective reductions of fatty materials occur using a catalyst consisting of essentially a zerovalent nickel dispersed on a support which shows strong metal, support interaction. A particularly desirable catalyst is one where the nickel is dispersed on titania which is subsequently activated in hydrogen at a temperature above about 325° C. The catalyst is sufficiently selective so as to permit continuous reduction of fatty materials using a fixed bed of catalyst.
45   U.S. Patent No. 4,424,162 discloses that hydrogenation of fatty materials using zerovalent platinum group metals supported on alpha-alumina are substantially more selective than those where the metal is supported on a porous alumina. An alpha-alumina with surface area less than about 5m²/g, a micropore volume under about 0.05 ml/g, and a macropore volume less than about 0.25 ml/g is particularly desirable. Using these methods, continuous hydrogenations based on a fixed bed process are sufficiently selective to
50 be commercially practicable.

U.S. Patent No. 4,479,902 discloses that selective reductions of fatty materials occur using a catalyst comprising zerovalent platinum or palladium dispersed on a support which shows strong metal-support interaction. A particularly desirable catalyst is one where the platinum or palladium is dispersed on titania which is subsequently activated in hydrogen at a temperature above about 325° C. The catalyst is sufficiently selective so as to permit continuous reduction of fatty materials using a fixed bed of catalyst.

U.S. Patent No. 4,510,092 discloses that a method of continuously hydrogenating fatty materials over a fixed catalyst bed utilizes zerovalent nickel on alpha-alumina. Partial hydrogenation of soybean oil to an IV of about 110 can be successfully performed using alpha-alumina of surface area less than about 5m²/g to afford a product whose SFI is acceptable for end product use.

U.S. Patent No. 4,510,091 discloses that selective continuous hydrogenations of fatty materials are possible over a fixed bed of zerovalent nickel on an alpha-alumina support. The selectivity of such continuous hydrogenations is further enhanced by performing such hydrogenations in an upflow mode. When soybean oil is used and hydrogenation is continued to an IV of about 110, the resulting partially hydrogenated soybean oil is comparable in its solids content to that obtained in a batch hydrogenation using presently conventional commercial catalysts.

U.S. Patent No. 4,547,319 discloses that a supported, phosphorus-modified zerovalent nickel catalyst shows improved selectivity in the hydrogenation of fatty materials. The increased selectivity ot this catalyst permits continuous reduction of fatty materials with a selectivity comparable to that observed in batch reduction using a more conventional nickel catalyst.

SUMMARY OF THE INVENTION

Hydrogenation of moderate to high selectivity edible oil products is accomplished utilizing particular catalyst loading. temperature control, liquid hydrogen and hydrogen flow control. According to the invention maximum product conversion is achieved by operating the reactor with vaporized liquid hydrogen injected into the reactor while raising the reactor temperature to the maximum operating temperature as quickly as possible and thereafter maintaining the reactor isothermally at the maximum temperature until the iodine value (IV) desired for the particular product is achieved.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic representation of a conventional batch hydrogenated reactor.

Figure 2 is a plot of catalytic activity against reaction time for a conventional hydrogenation reactor using reformer hydrogen and liquid hydrogen.

Figure 3 is a plot of product conversion as a function temperature for any irreversible reaction.

DETAILED DESCRIPTION OF THE INVENTION

To understand the present invention, it is critical to understand the present status of hydrogenation process in the art and the problems experienced in carrying out these processes. Hydrogenation is the addition of hydrogen to the ethylenic linkages present at the unsaturated double bonds of the fatty acids in the presence of a metal catalyst (e.g., nickel).

Most commercial hydrogenation is performed as a batch operation;

Figure 1 shows a typical batch hydrogenation reactor. The batch reactor or convertor consists of a tall cylindrical pressure vessel equipped with agitation, heating and cooling coils. The variable which must be controlled to give a specific end product are temperature, agitation, pressure, catalyst concentration as well as catalyst type. Hydrogen gas is fed to the vessel through a sparge ring at the lower part of the vessel. The hydrogen gas reacts with the double bonds of the unsaturated oil as the hydrogen is fed to the liquid phase. The hydrogen consumption rate depends on the operating conditions of the convertor. Hydrogen which is not reacted in the liquid phase passes to the headspace of the reactor where it is remixed with the oil for further reaction. Pressure in the reactor is controlled and maintained by a bent valve in the gas headspace which is typically manually opened to relieve high pressure. In practice, to prevent buildup of inert in the headspace, the reactors are vented throughout the reaction, thus losing some of the gas-phase hydrogen. This loss of hydrogen typically represents about 20 to 30% of the total consumption.

Most hydrogenators produce their own hydrogen by natural gas reforming. The older reformer systems, those built before 1980, typically have MEA and methanation cleanup systems. The newer ones use pressure swing adsorption (PSA) to remove the impurities. The purity of the reformer hydrogen is normally

very high, i.e. 97 to 99%. However, there are still trace amounts of contaminants, e.g. CO, O_2, sulfur compounds, etc., in the gas. These contaminants react with the nickel and deactivate the catalyst. Carbon monoxide and oxygen react with nickel (Ni) to form NiCO and NiO, respectively. NiO is reduced to Ni in the hydrogenation environment. However, this would lengthen the induction period. NiCO is reversible at reaction temperatures above 420°F. which are outside the temperature limit of the majority of the edible oil hydrogenation processes. Sulfur compounds (e.g., H_2S, SO_2) react irreversibly with Ni. Hydrogen from a liquid hydrogen source (LHY) is essentially free of these contaminants and thus will not deactivate the catalyst. A comparison of reformer and liquid source hydrogen is provided in the following table:
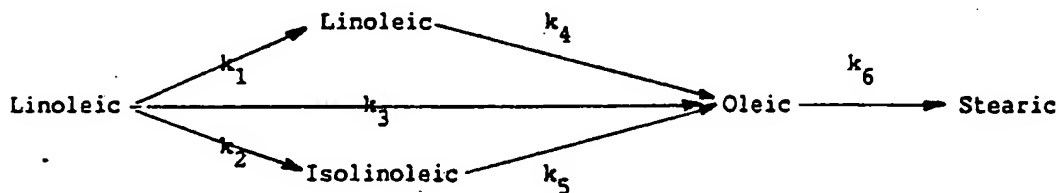
HYDROGEN PURITY COMPARISON

	Reformer and MEA Methanation	Typical Liquid
Hydrogen	97.92%	99.9999%
Oxygen	1.7 ppm	0.05 ppm
Nitrogen	1040 ppm	0.05 ppm
Methane	18200 ppm	0.05 ppm
Carbon Monoxide	1260 ppm	0.05 ppm
Carbon Dioxide	236 ppm	0.05 ppm
Moisture	38 ppm	0.05 ppm

When the hydrogenator is switched from reformer hydrogen to hydrogen from a LHY source, the catalyst deactivation rate is greatly reduced because of purity. Unfortunately, since hydrogenation reactions are exothermic, the high catalyst activity results in an increase in reactor temperature which is detrimental to the product specification. If the catalyst loading is reduced arbitrarily and/or the other operating parameters are not adjusted accordingly, the initial reactivity may be too low and the product specification will suffer.

The present invention provides the correlations needed to optimize and control the process for conversions from reformer hydrogen to LHY source hydrogen.

The present invention also provides the technology needed to optimize the use of LHY in hydrogenation by correlating the effects of catalyst loadings, starting temperatures, maximum allowable temperatures, and hydrogen consumption rates.

The reactions in the hydrogenation of an edible oil can be represented by the following schemes:

$$\text{Linoleic} \xrightarrow{k_1} \text{Linoleic} \xrightarrow{k_4} \text{Oleic} \xrightarrow{k_6} \text{Stearic}$$
$$\text{Linoleic} \xrightarrow{k_3} \text{Oleic}$$
$$\text{Linoleic} \xrightarrow{k_2} \text{Isolinoleic} \xrightarrow{k_5} \text{Oleic}$$

As shown in Figure 2, catalytic activity decreases rapidly when reformer H_2 is used (line AD). LHY source hydrogen, which is essentially free of contaminants, demonstrate much less catalyst deactivation (line AC). To obtain the same catalytic activity at point C with reformer H_2, a larger amount of catalyst has to be used in (line BC).

In addition to the catalyst concentration, the above reactions are also governed by the temperature. The overall conversion rate will increase with either increasing catalyst concentration or temperature. However, at high temperatures, the equilibrium concentration of the final products may shift and the product may not meet the specification. For instance, at high temperatures, the formation of linoleic and isolinoleic is favored over that of oleic acid.

Figure 3 further illustrates the relationship of conversion of a compound as a function of temperature where the reaction is irreversible, (i.e. A→B→C) where A is starting material B is the desired product and C

is unwanted by-product. In an irreversible stepwise reaction, the maximum amount of the intermediate product B being converted is dictated by the thermoequilibrium curve. At the point where the energy and material balance curves meet is the optimal point (T_o). At this condition, the maximum amount of conversion of B is achieved. At a higher temperature (T_H) conversion of B may actually be reduced.

In summary, the present invention is an improvement to a process for the hydrogenation of unsaturated edible oils to produce moderate and high selective products. The basic process involves the contacting of an unsaturated oil with hydrogen in the presence of a metal catalyst at elevated temperature and pressure. The improvement to the process is a method of operation wherein liquid hydrogen source hydrogen is utilized; the catalyst concentration and the starting and maximum operating temperature is determined by the product selectivity, and the temperature ramping used to increase the operating temperature from the starting to the maximum temperature is as rapid as possible for the reactor.

In the process of the present invention, the catalyst concentration for a moderate selectivity product is in the range of 50-60 ppm and in the range of 70-110 ppm for a high selectivity product.

The starting temperature is in the range of 260-280° F for the moderate selectivity product and 290-320° F for the high selectivity product. The starting temperature should be set as high as possible. However, it should not exceed the temperature at which the thermal reaction becomes significant. Depending upon product selectivity and final iodine value (IV) desired the maximum temperature at which the reactor operates will be between 300-500° F.

The temperature ramping should be 8° F/min. or greater from the initial temperature up to the maximum desired operating temperatures of the reactor. Once the catalyst reaction has started, it is important to increase the reactor temperature to the maximum allowable temperature as quickly as possible by adding external heat (or steam), if necessary.

It is critical to maintain an isothermal condition at the maximum operating temperature, otherwise, the selectivity of the product may suffer.

The hydrogen inlet flow rate should be measured and compared with the predicted rate of hydrogen consumption for a given oil. The rate of hydrogen consumption for a given oil is obtained by plotting the rate of change of the IV against time. If the flow rate is lower than the predicted value, the vent valve will be opened to permit more hydrogen to flow into the reactor. If the flow rate is higher than the predicted value, the vent valve should be closed to show the rate of flow of hydrogen into the reactor. Thus, the physical loss of H_2 and total catalyst loading are minimized while the mass transfer is being maximized.

The process starts by mixing the oil and the catalyst together in a batch reactor. Once the oil and catalyst are well mixed, the mixture is heated to the starting temperature and the hydrogen flow is initiated. After the hydrogen flow is initiated, the temperature should be raised as quickly as possible to the maximum temperature and maintained isothermally at that temperature. The reaction is allowed to run until the product IV (iodine value) has reached the target value for the specific product selected for the process.

The use of the present process results in a significant reduction in the amount of catalyst used and the time of reaction necessary to product the desired product. In addition the present process produces a more in-spec product.

As a demonstration of the efficacy of the process of the present invention the following examples were run.

Example 1

An edible unstaturated oil was hydrotreated to produce a moderate selectivity oil of the specification listed in Table I. in order to compare the present invention to the prior art processes, the hydrotreating test was run at least three times, each using a difference prior art process or the process of the present invention. Table I lists, in addition to the product oil specification, the product analysis and the pertinent operating conditions of the processes (values shown are averaged for multiple runs). As one can see from Table I, the process of the present invention results in a more in-spec product.

TABLE I

MODERATE SELECTIVITY PRODUCT #1

Product Specification	Saturated Fat Index (SFI)				Iodine Value	Starting Temp: F	Maximum Temp: F	Reaction Time: Min	Temp Ramp F/Min
	50	70	80	92					
Product Specification	22				85				
Product Produced with Conventional Technology with Reformer Hydrogen	23.7	11.35	7.5	3.5	81	260	300	50	5
Product Produced with Conventional Technology with Liquid Hydrogen	27.1	13.75	9.5	3.6	78.05	260	300	50	5
Product Produced with Process of Present Invention with Liquid Hydrogen	20.85	8.8	4.8	0.7	83.4	260	300	45	10

Example II

5   An edible unsaturated oil was hydrogenated to produce a second moderate selectivity oil of the specification listed in Table II. In order to compare the present invention, like in Example I, the hydrotreating test was run at least three times, each using a difference prior art process or the process of the present invention. Table II lists, in addition to the product oil specification, the product analysis and the pertinent operating conditions of the processes (value shown are averaged for multiple runs). As one can see from
10   Table II, the process of the present invention results in a more in-spec product.

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TABLE II

MODERATE SELECTIVITY PRODUCT #2

	Saturated Fat Index (SFI)				Iodine Value	Starting Temp: F	Maximum Temp: F	Reaction Time: Min	Temp Ramp F/Min
	50	70	80	92					
Product Specification	34-38	16-20	8-12	-	74-78				
Product Produced With Conventional Technology with Reformer Hydrogen	36.55	20.05	11.4	1.8	73.75	300	440	80	5
Product Produced With Conventional Technology With Liquid Hydrogen	39.25	22.75	15.2	4.05	75.95	300	440	80	5
Product Produced With Process of Present Invention With Liquid Hydrogen	36.0	19.4	12.7	3.6	77.2	300	440	65	12

Example III

Finally, an edible unsaturated oil was hydrotreated to produce a high selectivity oil of the specification listed in Table III. In order to compare the present invention, as in Examples I and III, the hydrotreating test was run at least three times, each using a difference prior art process or the process of the present invention. Table III lists, in addition to the product oil specification, the product analysis and the pertinent operating conditions of the processes (values shown are averaged for multiple runs). As one can see from Table III, the process of the present invention results in a more in-spec product.

TABLE III

HIGH SELECTIVITY PRODUCT

	Saturated Fat Index (SFI)					Starting Temp: F	Maximum Temp: F	Reaction Time: Min	Temp. Ramp: F/Min
	50	60	80	92	105				
Product Specification	57-61	46-49	N/A	19-23	N/A				
Product Produced With Conventional Technology With Reformer Hydrogen	61.1	48.05	42.25	24.1	5.0	300	470	90	5
Product Produced With Conventional Technology With Liquid Hydrogen	62.35	50.65	45.85	28.7	8.55	300	470	90	5
Product Produced With Process of Present Invention With Liquid Hydrogen	58.5	46.05	39.0	23.25	6.45	300	470	75	12

To summarize the results of the three examples, Table IV provides a comparison between the conventional process and the process of the present invention. The data in Table IV clearly show that the process of the present invention results, in addition to a more in-spec product as shown in Table I-III, in a significant reduction in reaction time and catalyst concentration.

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TABLE IV

OPERATION PARAMETERS

Product	Process	Starting Temp: F	Maximum Temp: F	F/Min (Ave)	Pressure PSIG	Reaction Time:Min.	Catalyst Conc: PPM	Present Invention Catalyst Reduction (%)
Moderate Selectivity #1	Conventional	260	300	5	65	50	66	-
	Present Invention	260	300	10	65	45	48	73
Moderate Selectivity #2	Conventional	300	440	5	30	80	56	-
	Present Invention	300	440	12	30	65	44	79
High Selectivity	Conventional	300	470	5	30	90	127	-
	Present Invention	300	470	12	30	75	85	67

The present invention has been described with reference to several specific embodiments thereof. These embodiments should not be viewed as a limitation on the present invention the scope of which should be ascertained by the following claims.

Claims

1. In a process for the hydrogenation of unsaturated oils to produce moderate or high selectivity edible oils, where the unsaturated oil is reacted with hydrogen in the presence of a metal catalyst, the improvement comprising the steps of:
utilizing hydrogen withdrawn as liquid from a suitable receptacle, vaporized and injected for reaction with the unsaturated oil; maintaining the catalyst concentration in a range of between 50 and 110 ppm; selecting a starting temperature for the reactor between 260° and 320°F; increasing the reactor temperature to a maximum operating temperature of between 300° and 500°F at a rate greater than 8°F/min. once the catalytic reaction has started; and maintaining the hydrogen flow rate at a level to achieve total hydrogen required for the reaction by controlling hydrogen venting from the reaction.

2. A process according to Claim 1 wherein the catalyst concentration is between 50 and 60 ppm and the starting temperature is between 260 and 280°F.

3. A process according to Claim 1 wherein the catalyst concentration is between 75 and 100 ppm and the starting temperature is between 290 and 320°F.

4. A process according to Claim 1 wherein the reactor proceeds until the iodine value of the product has reached its desired value for the unsaturated oil being hydrogenated.

FIG.1
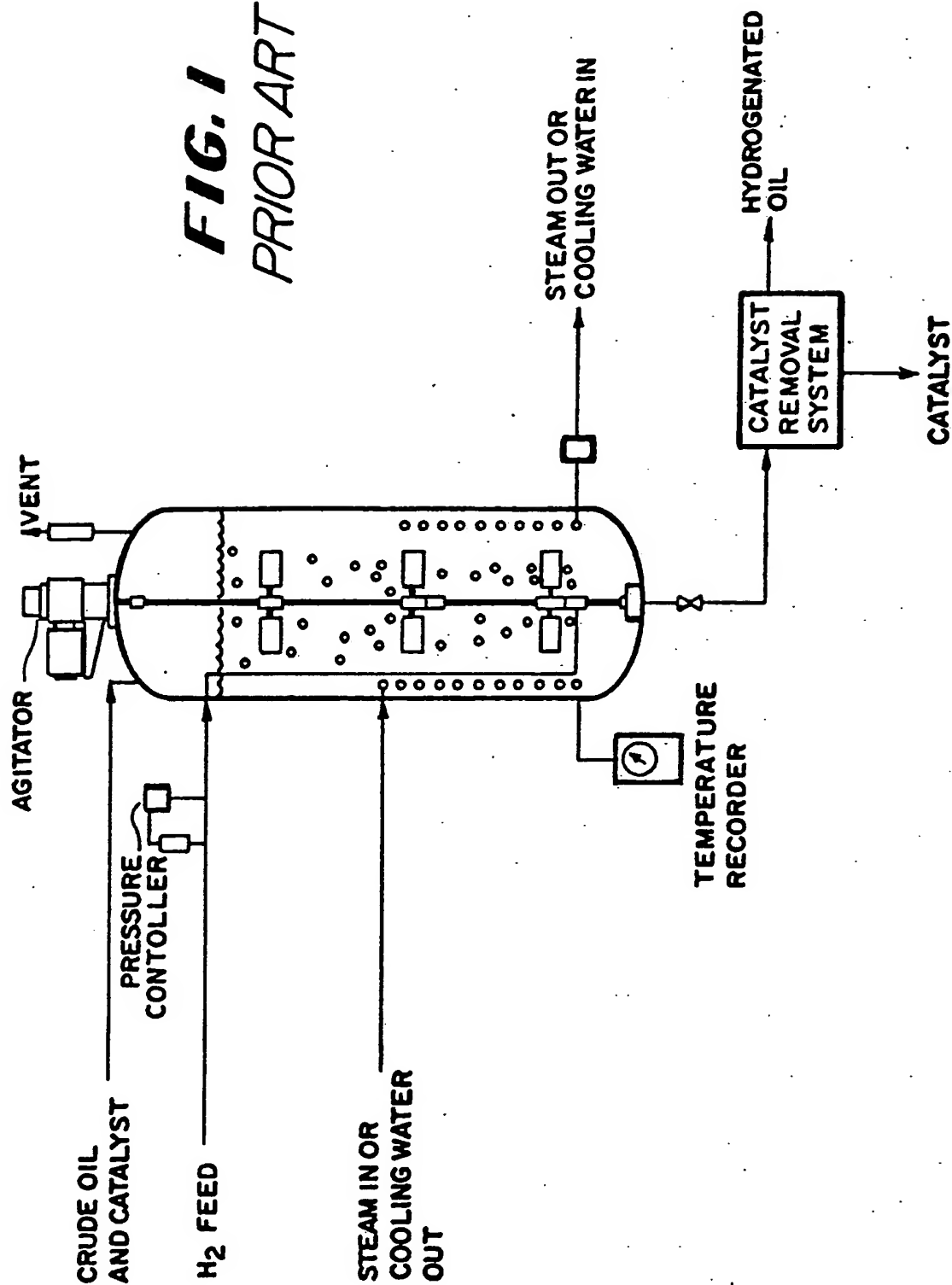PRIOR ART
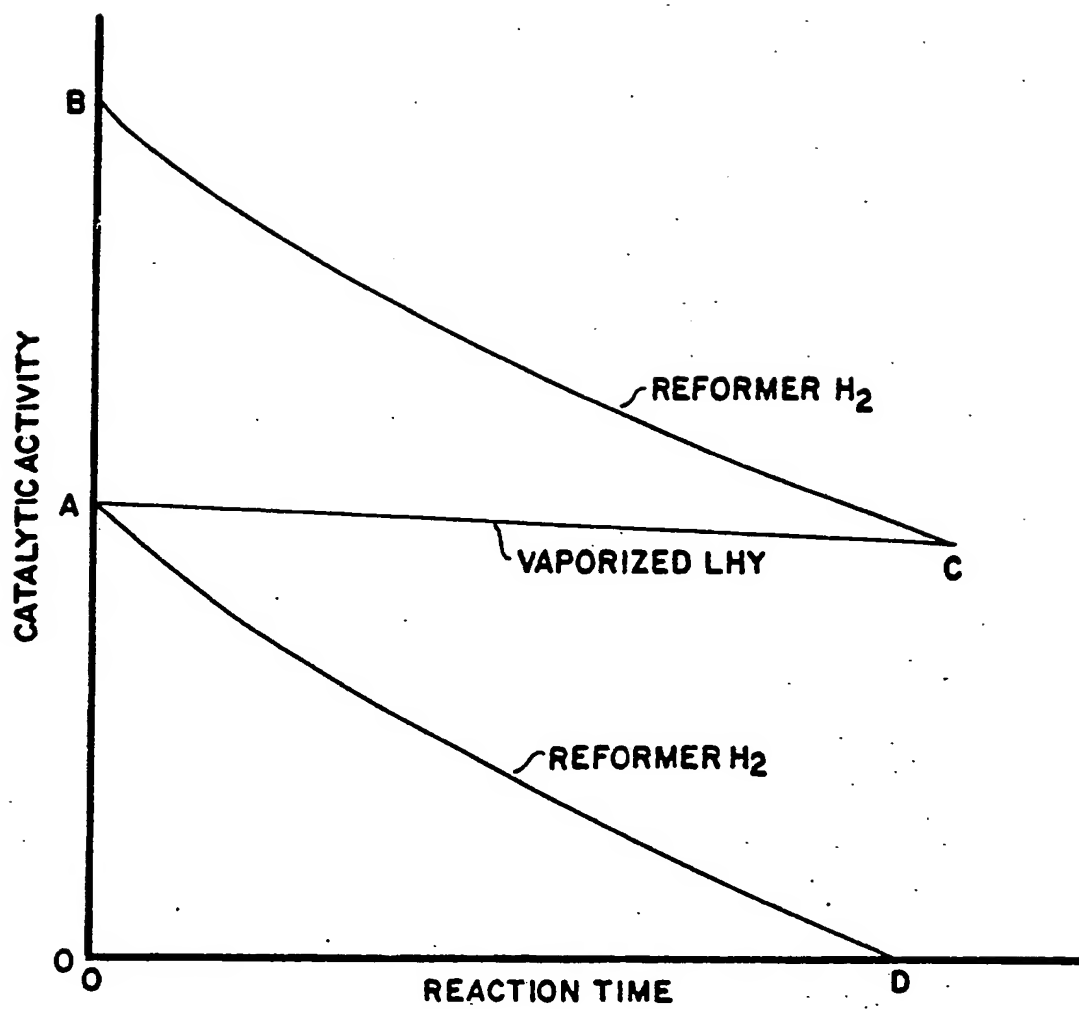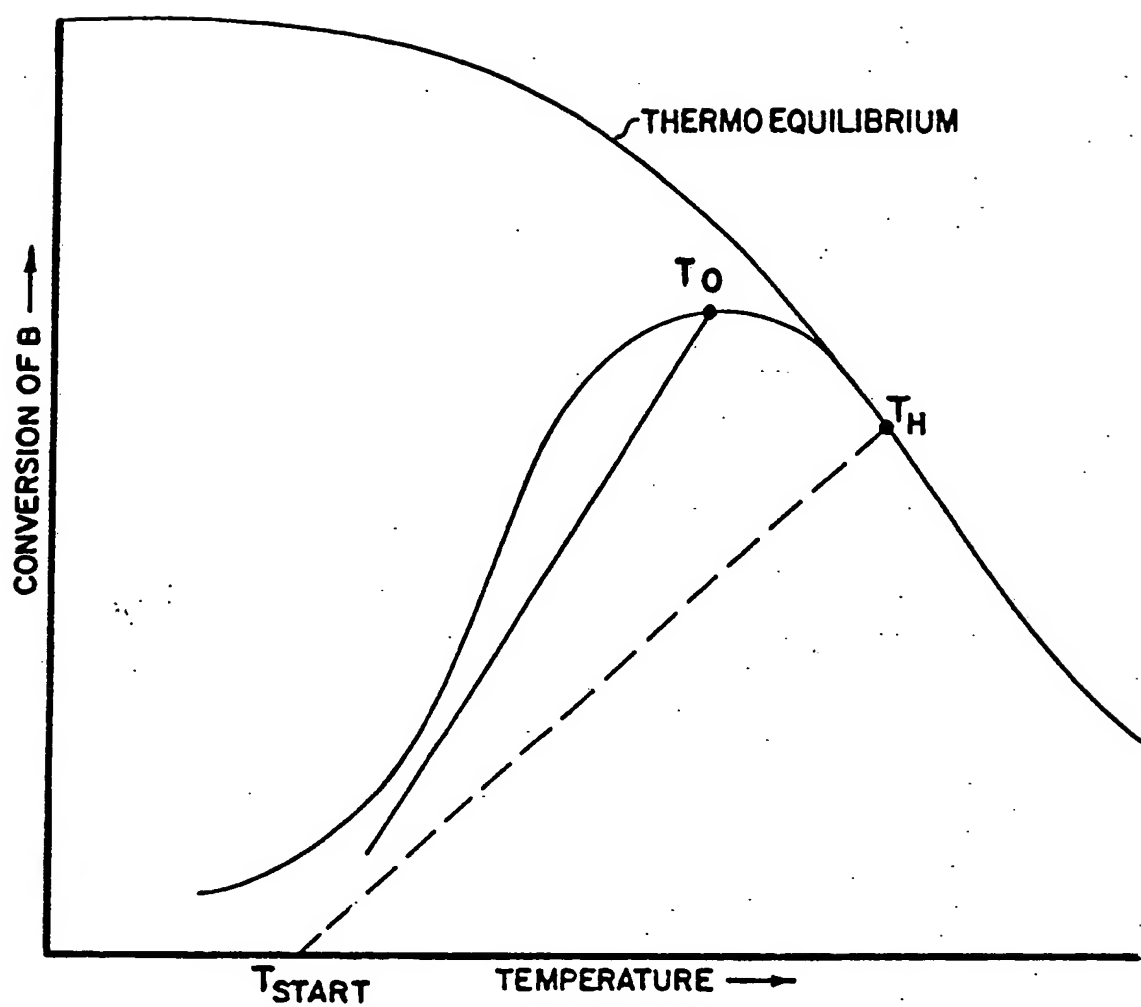
FIG. 2

FIG. 3